CLAIMS

We Claim:

1. A catalyst composition comprising, in combination, a polymerization catalyst and a carboxylate metal salt.

2. The catalyst composition of claim 1 wherein the polymerization catalyst comprises a conventional-type transition metal catalyst compound.

3. The catalyst composition of claim 1 wherein the polymerization catalyst comprises a bulky ligand metallocene-type catalyst compound.

4. The catalyst composition of a claim 1 wherein the carboxylate metal salt is represented by the formula:

$$MQ_X(OOCR)_y$$

where M is a metal from the Periodic Table of Elements; Q is halogen, or a hydroxy, alkyl, alkoxy, aryloxy, siloxy, silane or sulfonate group; R is a hydrocarbyl radical having from 2 to 100 carbon atoms; x is an integer from 0 to 3; y is an integer from 1 to 4; and the sum of x and y is equal to the valence of the metal M.

5. The catalyst composition of claim 4 wherein M is a metal from Groups 1 to 7 and Groups 13 to 16; Q is halogen or a hydroxy group; and R is a hydrocarbyl radical having from 4 to 24 carbon atoms.

6. The catalyst composition of claim 4 wherein y is either 1 or 2, M is a Group 2 or 13 metal, Q is a hydroxy group, and R is a hydrocarbyl radical having greater than 12 carbon atoms.

7. The catalyst composition of claim 1 wherein the carboxylate metal salt is selected from the group consisting of aluminum mono-stearate, aluminum di-stearate and aluminum tri-stearate or a combination thereof.

8. The catalyst composition of claim 1 wherein the polymerization catalyst comprises a carrier.

9. The catalyst composition of claim 1 wherein the weight percent of the carboxylate metal salt based on the total weight of the polymerization catalyst is in the range of from 0.5 weight percent to about 100 weight percent.

10. A method of making a catalyst composition, the method comprising the steps of combining:
(a) a polymerization catalyst; and
(b) a carboxylate metal salt.

11. The method of claim 10 wherein the polymerization catalyst comprises a conventional-type transition metal catalyst compound.

12. The method of claim 10 wherein the polymerization catalyst comprises a bulky ligand metallocene-type catalyst compound.

13. The method of a claim 10 wherein the polymerization catalyst comprises a carrier.

14. The catalyst composition of a claim 10 wherein the carboxylate metal salt is represented by the formula:

$$MQ_X(OOCR)_y$$

where M is a metal from the Periodic Table of Elements; Q is halogen, or a hydroxy, alkyl, alkoxy, aryloxy, siloxy, silane or sulfonate group; R is a hydrocarbyl radical having from 2 to 100 carbon atoms; x is an integer from 0 to 3; y is an integer from 1 to 4; and the sum of x and y is equal to the valence of the metal M.

15. The method of claim 10 wherein the polymerization catalyst comprises a carrier, an activator, and a bulky ligand metallocene-type catalyst compound.

16. The method of claim 10 wherein the weight percent of the carboxylate metal salt based on the total weight of the polymerization catalyst is in the range of from 1 weight percent to about 20 weight percent.

17. The method of claim 10 wherein the polymerization catalyst and the carboxylate metal salt are solids.

18. The method of claim 10 wherein the carboxylate metal salt is selected from the group consisting of aluminum mono-stearate, aluminum di-stearate and aluminum tri-stearate or combination thereof.

19. The method of claim 15 wherein the weight percent of the carboxylate metal salt based on the total weight of the polymerization catalyst is in the range of from 0.5 weight percent to about 25 weight percent.

20. A method of making a catalyst composition, the method comprising the steps of:

    (a) forming a polymerization catalyst; and
    (b) adding at least one carboxylate metal salt.

21. The method of claim 20 wherein the polymerization catalyst comprises a conventional-type transition metal catalyst compound.

22. The method of claim 20 wherein the polymerization catalyst comprises a bulky ligand metallocene-type catalyst compound.

23. The method of claim 20 wherein the polymerization catalyst comprises a carrier.

24. The method of claim 20 wherein the polymerization catalyst comprises an inorganic carrier.

25. The method of claim 20 wherein the polymerization catalyst and the at least one carboxylate metal salt are contacted for a period of time from about 1 minute to about 12 hours prior to using the catalyst composition in a polymerization process.

26. The method of claim 20 wherein the weight percent of the at least one carboxylate metal salt based on the total weight of the polymerization catalyst is in the range of from 0.5 weight percent to about 25 weight percent.

27. The method of claim 23 wherein the weight percent of the at least one carboxylate metal salt based on the total weight percent of the polymerization catalyst is in the range of from about 2 to about 20 weight percent.

28. The method of claim 20 wherein the polymerization catalyst formed is a supported bulky ligand metallocene-type catalyst system that is substantially dry and free flowing, and the at least one carboxylate metal salt is contacted with the supported bulky ligand metallocene-type catalyst system.

29. The method of claim 28 wherein the at least one carboxylate metal salt is a stearate compound.

30. A method of making a catalyst composition, the method comprising the step of mixing a preformed, solid free flowing supported bulky ligand metallocene-type catalyst system with a carboxylate metal salt.

31. The method of claim 30 wherein the weight percent of the carboxylate metal salt based on the total weight of the supported bulky ligand metallocene-type catalyst system is in the range of from about 0.5 to about 25 weight percent.

32. The method of claim 30 wherein the carboxylate metal salt has a melting point in the range of from about 100 °C to about 200 °C.

33. The method of claim 30 wherein the supported bulky ligand metallocene-type catalyst system comprises a bulky ligand metallocene-type catalyst compound represented by the formula:

$$(C_5H_{4-d}R_d)\ A_x\ (C_5H_{4-d}R_d)\ M\ Qg\text{-}2$$

wherein M is a Group 4, 5 , 6 transition metal, $(C_5H_{4-d}R_d)$ is an unsubstituted or substituted cyclopentadienyl derived bulky ligand bonded to M, each R, which can be the same or different, is hydrogen or a substituent group containing up to 50 non-hydrogen atoms or substituted or unsubstituted hydrocarbyl having from 1 to 30 carbon atoms or combinations thereof , or two or more carbon atoms are joined together to form a part of a substituted or unsubstituted ring or ring system having 4 to 30 carbon atoms, A is one or more of, or a combination of carbon, germanium, silicon, tin, phosphorous or nitrogen atom containing radical bridging two $(C_5H_{4-d}R_d)$ rings; each Q which can be the same or different is a hydride, substituted or unsubstituted, linear, cyclic or branched, hydrocarbyl having from 1 to 30 carbon atoms, halogen, alkoxides, aryloxides, amides, phosphides, or any other univalent anionic ligand or combination thereof; also, two Q's together may form an alkylidene ligand or cyclometallated hydrocarbyl ligand or other divalent anionic chelating ligand, where g is an integer corresponding to the formal oxidation state of M, and d is an integer selected from the 0, 1, 2, 3 or 4 and denoting the degree of substitution and x is an integer from 0 to 1.

34. The method of claim 33 wherein x is 1 and the weight percent of the carboxylate metal salt based on the total weight percent of supported bulky ligand metallocene-type catalyst system is in the range of from about 0.5 to about 25 weight percent.

35. The method of claim 33 wherein the ratio of the weight of the carboxylate metal salt to the weight of the transition metal is in the range of from about 1 to about 100.

36. The method of claim 30 wherein the mixing period of time is from about 1 minute to about 12 hours and the supported bulky ligand metallocene-type catalyst system is supported on an inorganic oxide.

37. The method of claim 30 wherein the mixing period of time is from 10 minutes to about 10 hours.

38. The method claim 30 wherein the mixing period of time is from 30 minutes to about 8 hours.

39. The method of claim 30 wherein the carboxylate metal salt is selected from the group consisting of aluminum mono-stearate, aluminum di-stearate and aluminum tri-stearate or combination thereof.

40. A process for polymerizing olefin(s) in the presence of the catalyst composition of claim 1.

41. A process for polymerizing olefin(s) in the presence of the catalyst composition of claim 10.

42. A process for polymerizing olefin(s) in the presence of the catalyst composition of claim 20.

43. A process for polymerizing olefin(s) in the presence of the supported catalyst composition of claim 30.

44. A process for polymerizing olefin(s) in the presence of the supported catalyst composition of claim 34.

45. A process for polymerizing olefin(s) in a reactor in the presence of a catalyst composition comprising a polymerization catalyst having been contacted prior to its introduction into the reactor with a carboxylate metal salt.

46. The process of claim 45 wherein the polymerization catalyst comprises a bulky ligand metallocene-type catalyst compound.

47. The process of claim 45 wherein the polymerization catalyst comprises a conventional-type transition metal catalyst compound.

48. The process of claim 45 wherein the polymerization catalyst comprises a carrier.

49. The process of claim 45 wherein the polymerization catalyst comprises an inorganic carrier and a bulky ligand metallocene-type catalyst compound, and the weight percent of the carboxylate metal salt based on the total weight percent of polymerization catalyst is in the range of from about 0.5 to about 25 weight percent.

50. A gas phase or slurry phase process for polymerizing olefin(s) in a reactor in the presence of a catalyst composition, the catalyst composition comprising at least one polymerization catalyst and at least one carboxylate metal salt.

51. The process of claim 50 wherein the process is a gas phase process and the reactor is a fluid bed reactor.

52. The process of claim 51 wherein the at least one polymerization catalyst comprises a bulky ligand metallocene-type catalyst compound and an activator.

53. The process of claim 50 wherein the process is producing a polymer product having a density greater than 0.920 g/cc and a melt index less than about 1 dg/min.

54. The process of claim 50 wherein the process is producing a polymer product having a density greater than 0.925 g/cc and a melt index less than 0.75 dg/min.

55. The process of claim 51 wherein the process is producing greater than 1000 lbs (455 Kg) of a polymer product per hour.

56. The process of claim 55 wherein the at least one polymerization catalyst comprises an inorganic carrier, a bulky ligand metallocene-type catalyst compound and an activator.

57. The process of claim 50 wherein the at least one polymerization catalyst comprises a bulky ligand metallocene-type catalyst compound represented by the formula:

$$(C_5H_{4-d}R_d)\ A_x\ (C_5H_{4-d}R_d)\ M\ Qg\text{-}2$$

wherein M is a Group 4, 5, 6 transition metal, $(C_5H_{4-d}R_d)$ is an unsubstituted or substituted cyclopentadienyl derived bulky ligand bonded to M, each R, which can be the same or different, is hydrogen or a substituent group containing up to 50 non-hydrogen atoms or substituted or unsubstituted hydrocarbyl having from 1 to 30 carbon atoms or combinations thereof , or two or more carbon atoms are joined together to form a part of a substituted or unsubstituted ring or ring system having 4 to 30 carbon atoms, A is one or more of, or a combination of carbon, germanium, silicon, tin, phosphorous or nitrogen atom containing radical bridging two $(C_5H_{4-d}R_d)$ rings; each Q which can be the same or different is a hydride, substituted or unsubstituted, linear, cyclic or branched, hydrocarbyl having from 1 to 30 carbon atoms, halogen, alkoxides, aryloxides, amides, phosphides, or any other univalent anionic ligand or combination thereof; also, two Q's together may form an alkylidene ligand or cyclometallated hydrocarbyl ligand or other divalent anionic chelating ligand, where g is an integer corresponding to the formal oxidation state of M, and d is an integer selected from the 0, 1, 2, 3 or 4 and denoting the degree of substitution and x is an integer from 0 to 1.

58. The process of claim 57 wherein x is 1 and the process is producing a polymer product having a I_{21}/I_2 of greater than 30.

59. The process of claim 58 wherein the weight percent of the at least one carboxylate metal salt is greater than 1 based on the total weight of the at least one polymerization catalyst, and the polymer product having a density greater than 0.910 g/cc.

60. The process of claim 57 wherein x is 1 and process is producing a propylene homopolymer or a propylene copolymer.

61. The process of claim 50 wherein the at least one polymerization catalyst composition comprises a conventional-type transition metal catalyst compound represented by the formula:

$$MR_X$$

where M is a metal from Groups IIIB to VIII, R is halogen or a hydrocarbyloxy group; and x is equal to the valency of the metal.

62. The process of claim 61 wherein the process is producing a polymer product having a composition distribution breadth index of less than 50 percent.

63. The process of claim 50 wherein the at least one polymerization catalyst comprises alumoxane or an aluminum alkyl as an activator or a cocatalyst.

64. The process of claim 50 wherein the at least one carboxylate metal salt is represented by the formula:

$$MQ_X(OOCR)_y$$

where M is a metal from the Periodic Table of Elements; Q is halogen, or a hydroxy, alkyl, alkoxy, aryloxy, siloxy, silane or sulfonate group; R is a hydrocarbyl radical having from 2 to 100 carbon atoms; x is an integer from 0 to 3; y is an integer from 1 to 4; and the sum of x and y is equal to the valence of the metal M.

65. The process of claim 64 wherein M is a metal from Groups 1 to 7 and Groups 13 to 16; Q is halogen or a hydroxy group; and R is a hydrocarbyl radical having from 2 to 24 carbon atoms.

66. The process of claim 64 wherein y is either 1, 2 or 3, M is a Group 2 or 13 metal, Q is a hydroxy group, and R is a hydrocarbyl radical having greater than 12 carbon atoms.

67. The process of claim 50 wherein the at least one carboxylate metal salt is selected from the group consisting of aluminum mono-stearate, aluminum di-stearate and aluminum tri-stearate or combination thereof.

68. The process of claim 50 wherein the at least one polymerization catalyst comprises a carrier.

69. The process of claim 68 wherein the catalyst composition has a productivity greater than 1500 grams of a polymer produced per gram of the catalyst composition.

70. A continuous gas phase process for polymerizing monomer(s) in a reactor, said process comprising the steps of:
    (a) introducing a recycle stream into the reactor, the recycle stream comprising one or more monomer(s);
    (b) introducing a polymerization catalyst and a carboxylate metal salt into the reactor;
    (c) withdrawing the recycle stream from the reactor;
    (d) cooling the recycle stream;
    (e) introducing into the reactor additional monomer(s) to replace the monomer(s) polymerized;
    (g) reintroducing the recycle stream into the reactor; and
    (h) withdrawing a polymer product from the reactor.

71. The process of claim 70 wherein the polymerization catalyst comprises a bulky ligand metallocene-type catalyst compound and an activator.

72. The process of claim 71 wherein the polymerization catalyst comprises a carrier and the polymerization catalyst is solid and free flowing.

73. The process of claim 70 wherein the polymerization catalyst comprises a conventional-type transition metal catalyst compound and a cocatalyst.

74. The process of claim 70 wherein the process further comprises the step of alternating the polymerization catalyst with another polymerization catalyst.

75. The process of claim 70 wherein the polymerization catalyst and the carboxylate metal salt are introduced continuously or intermittently into the reactor.

76. The process of claim 70 wherein the polymer product has a density greater than 0.920 g/cc and a I_{21}/I_2 greater than 30.

77. The process of claim 70 wherein the polymer product has a density greater than 0.925 g/cc and a melt index less than 1 dg/min.

78. The process of claim 70 wherein the polymerization catalyst and the carboxylate metal salt are combined to form a catalyst composition prior to introducing the catalyst composition to the reactor.

79. The process of claim 70 wherein the recycle stream comprises a gas phase and a liquid phase.

80. The process of claim 79 wherein the liquid phase is introduced apart from the gas phase into the reactor or a separate liquid is introduced into the reactor.

81. The process of claim 70 wherein the polymer product is withdrawn at a rate greater than 1000 lbs (455 Kg) of the polymer product per hour.

82. The process of claim 70 wherein the polymer product is withdrawn at a rate greater than 25,000 lbs (11,340 Kg) of polymer product per hour.

83. The process of claim 82 wherein the polymer product has a melt index less than 1.

84. The process of claim 83 wherein the polymer product has density greater than 0.920 g/cc.

85. A process for polymerizing one or more olefins at least one of which is ethylene in the presence of a catalyst composition to produce a first polymer product, the catalyst composition comprising a first polymerization catalyst and a carboxylate metal salt.

86. The process of claim 85 wherein the first catalyst composition is utilized at start-up of the process, after the process has stabilized, a second polymerization catalyst substantially free of the carboxylate metal salt is utilized to produce a second polymer product.

87. The process of claim 86 wherein the second polymerization catalyst is the same as the first polymerization catalyst.

88. The process of claim 85 wherein the first polymer product has a density greater 0.920 g/cc and a melt index less than 1 dg/min.

89. The process of claim 86 wherein the first polymer product has a melt index less than 1 and the second polymer product has melt index greater than 1 dg/min.

90. A polymerization process for producing a first ethylene based polymer product having a density greater than 0.87 g/cc and a melt index greater than 1 dg/min in the presence of a first catalyst composition comprising a first polymerization catalyst, the process comprising the step of: transitioning to a second catalyst composition to produce a second ethylene based polymer product having a density greater than 0.920 g/cc and a melt index less than or equal to 1 dg/min, the second catalyst composition comprising a second polymerization catalyst and a carboxylate metal salt.

91. The process of claim 90 wherein the first polymerization catalyst and second polymerization catalyst comprise a bulky ligand metallocene-type catalyst compound.

92. The process of claim 90 wherein the first polymer product has a I_{21}/I_2 less than 25.

93. The process of claim 90 wherein the second polymer product has a I_{21}/I_2 greater than 30.

94. The process of claim 90 wherein the first and second polymer products have the same or similar density.

95. The process of claim 90 wherein the second polymerization catalyst comprises a carrier.

96. The process of claim 90 wherein the process is a gas phase process.

97. The process of claim 90 wherein the process is a slurry phase process.

98. The process of claim 90 wherein the first polymer product has a density greater than 0.910 g/cc and a melt index greater than 1.5 dg/min.

99. The process of claim 98 wherein the second polymer product has a density greater than 0.920 g/cc and a melt index less than 0.75 dg/min.

100. The process of claim 90 wherein the second polymerization catalyst comprises a bridged, bulky ligand metallocene-type catalyst compound and a carrier.

101. A continuous gas phase polymerization process for polymerizing ethylene and one or more alpha-olefins having 4 or more carbon atoms at a pressure in the range of from about 200 psig (1379 kPa) to about 400 psig (2759 kPa), a polymerization temperature in the range of from about 70 °C to about 110 °C, at a production rate of greater than 10,000 pounds (4540 Kg) of a polymer product per hour, and at a polymerization catalyst productivity of greater than 1500 grams of the polymer product per gram of the polymerization catalyst, the process operating in the presence of a carboxylate metal salt.

102. The process of claim 101 wherein the carboxylate metal salt is contacted with the polymerization catalyst to form a catalyst composition.

103. The process of claim 102 wherein the catalyst composition further comprises a carrier.

104. The process of claim 101 wherein the polymerization catalyst is a conventional-type transition metal catalyst compound.

105. The process of claim 101 wherein the polymerization catalyst is a bulky ligand metallocene-type catalyst compound.

106. The process of claim 101 wherein the polymerization catalyst is a bridged, bulky ligand metallocene-type catalyst compound.

107. The process of claim 101 wherein the carboxylate metal salt is introduced to the process continuously or intermittently.

108. The process of claim 101 wherein the production rate is greater than 25,000 pounds (11,340 Kg/hr) of the polymer product per hour.

109. The process of claim 101 wherein the polymerization catalyst has a productivity greater than 2000 grams of the polymer product per gram of the polymerization catalyst.

110. The process of claim 101 wherein the polymer product has an I_{21}/I_2 greater than 35 and density greater than 0.910 g/cc.

111. The process of claim 101 wherein the polymerization catalyst comprises a bulky ligand metallocene-type catalyst compound, an activator and a carrier, and the carboxylate metal salt is present in an amount based on the total weight of the polymerization catalyst in the range of from about 0.5 to about 100 weight percent.

112. The process of claim 111 wherein the carboxylate metal salt is represented by the formula:

$$MQ_X(OOCR)_y$$

where M is a metal from the Periodic Table of Elements; Q is halogen, or a hydroxy, alkyl, alkoxy, aryloxy, siloxy, silane or sulfonate group; R is a hydrocarbyl radical having from 2 to 100 carbon atoms; x is an integer from 0 to 3; y is an integer from 1 to 4; and the sum of x and y is equal to the valence of the metal M.

113. The process of claim 111 wherein the carboxylate metal salt is selected from the group consisting of aluminum mono-stearate, aluminum di-stearate and aluminum tri-stearate or a combination thereof.

114. The process of claim 111 wherein the polymer product has a I_{21}/I_2 greater than 25 and the polymerization catalyst productivity is greater than 2000 grams of the polymer product per gram of the polymerization catalyst.

115. The process of claim 111 wherein the polymerization catalyst productivity is greater than 3000 grams of the polymer product per gram of the polymerization catalyst, the bulky ligand metallocene-type catalyst compound is a bridged, bulky ligand metallocene-type catalyst compound, and the process is producing greater than 25,000 pounds (11,340 Kg) of a polymer product per hour.

116. A continuous process for polymerizing monomer(s) in a fluidized bed gas phase reactor operating under a pressure in the range of from about 200 psig (1379 kPa) to about 400 psig (2759 kPa) and a polymerization temperature in the range of from about 70 °C to about 110 °C, the process comprising the steps of:

(a) introducing a recycle stream into the reactor, the recycle stream comprising one or more monomer(s);

(b) introducing a polymerization catalyst comprising a bulky ligand metallocene-type catalyst compound, an activator and an inorganic carrier, and a carboxylate metal salt into the reactor;

(c) withdrawing the recycle stream from the reactor;

(d) cooling the recycle stream;

(e) introducing into the reactor additional monomer(s) to replace the monomer(s) polymerized;

(g) reintroducing the recycle stream into the reactor; and withdrawing greater than 10,000 pounds (4540 Kg) of a polymer product per hour from the reactor.

117. The process of claim 116 wherein the polymerization catalyst and the carboxylate metal salt are mixed to form a catalyst composition wherein the carboxylate metal salt is present in an amount based on the total weight of the polymerization catalyst in the range of from about 0.5 to about 100 weight percent.

118. The process of claim 116 wherein the polymerization catalyst comprises silica.

119. The process of claim 118 wherein the bulky ligand metallocene-type catalyst compound is a bridged, bulky ligand metallocene-type catalyst compound and the activator is alumoxane.

120. The process of claim 116 wherein the polymer product is withdrawn at a rate greater than 25,000 pounds (11,340 Kg/hr) of the polymer product per hour.